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Synthesis of MnO_2 nanowires adsorbent for gold recovery from electroplating wastewater using Taguchi method

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Abstract

In this study, MnO_2 nanowire adsorbent was synthesized by low cost preparation method that was capable of extracting gold form diluted jewellery waste water solutions. Different adsorption parameters like number of treatment, hold time, pH and agitation speed of mixing on the gold adsorption were studied. Adsorption experiments was designed by Taguchi method and effectiveness of parameters as well as optimum operating conditions were determined. The manganese oxide adsorbent, prepared by low-temperature synthesis followed by acid treatments, exhibits a nanowire like morphology. The results showed that under the optimum operating condition, gold adsorption efficiency was more than 77.2% during 2h.

Keywords: MnO_2 nanowire, electroplating wastewater, gold recovery, Taguchi.

1.Introduction

About 80 % of the metal annually involved into the gold market is used to the production of jewellery. In small workshops, where the jewellery is measured, finished, cleaned and polished and the waste was collected and then transferred to founders for the final treatment. This procedure had poor recovery, mainly due to the lack of chemical and morphological knowledge of the constituents of the waste. Jewellery workshops generate three different kind of waste: "handwashing waste", "jewellery polishing waste" and "floor sweepings waste" [1]. "Handwashing waste" is generated by the rubbish coming from handwashing of operators and clothes for laboratory cleaning. This waste constitutes 40.7 % of the total waste from craft workshops and an average gold 2.89 % [2]. "Jewellery polishing waste" is generated when the artifacts are cleaned and polished using bristles of different hardness running over their surfaces. It accounts for 26% of the total waste. Its gold content is 5.34 %. The "floor sweepings waste" contains the product of the floor sweeping. It accounts for 33% of the total waste. Its gold content is 1.20%.

Use of adsorbents to recover gold from waste water, due to the extreme dilution, requires effective suspension of the adsorbing particles with maximally allowed, chemically active sites and exceedingly high rate of Au(I) to Au(0) reduction. Previous methods of gold recovery were either feasible only to specially processed solutions containing rather high gold concentrations or deemed impractical due to low yields, operational difficulties or environmental concerns. More adsorbents such as silica-polymer composites [3-,4], surfactants [5], pyrite, goethite and birnessite [6,7] were used to adsorb gold ions from acidic solutions (pH < 4) or waste water containing 1–130 ppm of gold.

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Also, activated carbons and ion-exchange resins were used to recover gold ions from cyanide-leached solutions in the mining industry [8,9]. In addition, utilization of algae [10] and micro-organisms [11] were recommended for gold recovery [12]. Hence, an adsorbent capable of recovering gold from waste water down to ppm level with high efficacy and minimal environmental impact is highly desirable. Furthermore, cost consideration demands a relatively simple method of synthesis and chemical processing of the adsorbent [13, 14].

Our contemplation of a suitable manganese-oxide adsorbent was motivated by several important properties common to manganese oxide/hydroxide minerals: (i) the ubiquitous presence in the ocean floor, soils, and sediments, which imply environmental benignity [13]; (ii) the high cation-exchange capacity; and (iii) the available Mn(II), Mn(III) and Mn(IV) states that are amenable to oxidation–reduction reactions. However, the Mn(IV) oxidation state in MnO_2-type compounds is known to promote dissolution of gold in hydrochloric solutions.

Literature survey revealed that a few low cost and applied methods were used for gold recovery by nanoadsorbent. Therefore, in this study, MnO_2 adsorbent was synthesized and different adsorption parameters such as hold time, number of acid treatment, pH and agitation speed on the gold adsorption capacity via Taguchi method were studied.

2.Experimental

2.1. Preparation of adsorbent

2.1.1. Low-temperature synthesis and acid treatment

The $MnCO_3$ powder as the starting material was heated using an electric furnace at 230 ◦C for 4.5h. Then, an acid treatment was done with adding the powder into a 0.5mol/L of hydrochloric acid in the stirred glass vessel for definite time. Afterward the suspended particles were filtered from the solution followed by washing with distilled water.

2.2 Adsorption experiments

In these tests, feed solution was wastewater collected from a gold plated manufacture line containing 0.6-0.8mg gold in one liter solution. The effects of different parameters such as number of treatment, hold time, pH and agitation speed of solution were investigated. The process parameters and their levels are shown in Table 1. In the experiments, 0.01gr of adsorbent was added to 100 ml of gold solution in glass bottles. Samples were shaken at room temperature for the hold times. In all of experiments, pH of the solutions was adjusted using either NaOH (2M) or HCl (2M) solutions.

After that, the solution was filtered and gold concentration in the liquid was analyzed by atomic adsorption spectrophotometer (Unicam, model 939) with an air-acetylene flame and an adsorbance peak at a wavelength of 242.8 nm. The adsorbed gold with manganese oxide was determined by difference of gold concentrations in initial and final solution. To ensure the accuracy, reliability and reproducibility of collected data, all the adsorption experiments were carried out in duplicate and the mean value of two data set are presented.

2.3. Taguchi method

Taguchi method provides an efficient approach for conducting experiment during research and development to determine nearly optimum design parameters in view of performance and cost [15-21].

Adsorption tests were designed using Taguchi method and effectiveness of parameters as well as optimum operating condition was determined. In the present study, there are eight degrees of freedom related to the four sets of three-level adsorption parameters. In accordance with Taguchi method, the standard orthogonal array L9, with four columns and nine rows can be used to these experiments. The adsorption parameters and their levels are shown in Table 1. The experimental layout for these parameters using the L9 orthogonal array is listed in Table 2.

In the experiments, percent of final gold adsorption is selected as the response of the system in Taguchi method and optimum operating conditions is determined based on this parameter.

Table 1. Adsorption parameters and their levels.

Process parameter	Unit	Level 1	Level 2	Level 3
Number of Treatment		2	3	5
Hold time	min	120	180	300
Agitation speed	rpm	200	300	500
pH		3-4	5-6	8-9

Table 2. Arrangement of parameters in L9 orthogonal array.

Parameters	Number of treatment	Hold time	Agitation speed	pH
Experiment				
T1	5	3	200	8-9
T2	3	2	500	8-9
T3	5	5	500	3-4
T4	2	5	300	8-9
T5	3	3	300	3-4
T6	3	5	200	5-6
T7	2	2	200	3-4
T8	5	2	300	5-6
T9	2	3	500	5-6

3. Results and discussion

3.1. The SEM of manganese oxide

Fig. 1 shows SEM images of growth steps of Manganese oxide nanoparticles (MnO_2) around $MnCO_3$. Shapes of these nanoparticles were wire like and average their radius were nearly 100nm. Fig. 1(a) depicts irregular shape of $MnCO_3$ that was heated in electrical furnace at 230 ˚C for 4.5h. After twice acidic treatment, $MnCO_3$ was reduced to MnO_2 (Fig. 1(b)). Fallowing thrice acidic treatment, MnO_2 nanowire with average radius of 100nm is revealed in Fig. 1(c). Fifth acidic treatment led to well established MnO_2 nanowires (Fig. 1(d)).

3.2. Gold ions adsorption experiments

Table 3 shows the removal percentage of adsorption and adsorption capacity (q_e) of gold from electroplating wastewater by 0.01gr of adsorbent. These parameters were obtained as follows:

$$removal\% = \frac{C0-Ce}{C0} \times 100 \quad (1)$$

$$q_e = \frac{(C0-Ce)\times V}{m} \quad (2)$$

Where C_0 and C_e are the initial and final concentrations (mg/g) of metal ions in the aqueous solution, respectively, V (L) is the volume of metal ion solution, and m (g) is the weight of sorbent.

According to the Table 3, maximum percentage of gold adsorption occurs in T8 experiment at the value of 77.2%.

Fig. 2 to 5 shows adsorption capacity against the level of factors. The data of the Fig. 2 indicate adsorption capacity was maximum value of nearly 3.6 mg/g at pH=5-6. Adsorption capacity at different agitation speed was given in Fig.3. This figure shows that there is suitable adsorption capacity in the speed of 300rpm. Fig. 4. shows that effective adsorption capacity occur at hold time of 2h. Also, the effect of number of acid treatment on MnO_2 adsorption capacity was shown in Fig. 5. This figure depicts that the thrice acid treatment have the best effect on the gold adsorption process.

Based on the experimental studies described above, the optimal operating condition required for quantitative adsorption of gold ions with MnO_2 are as given below: *Thrice numbers of acid treatment, 2h hold time at pH 5-6 and an average speed of mixing at 300rpm.*

3.3. Analysis of the results by ANOVA table

Another step of Taguchi method is the analysis of results or ANOVA table. The purpose of the ANOVA data is to investigate which adsorption parameters significantly affect the performance characteristic and the contribution of each parameter on the adsorption efficiency. The percentage contribution of each parameter in the total sum of the squared deviations can

be used to evaluate the importance of the parameter change on the performance characteristic. In addition, the F-ratio can also be used to determine which parameters have a significant effect on the performance characteristic. The calculated values are then compared with F values predicted by statistical F distribution (in Fischer tables) [22], at 95% and at 99% confidence levels. According to the rule, when the F calculated in the ANOVA table is bigger than the standard F, the parameter is significantly

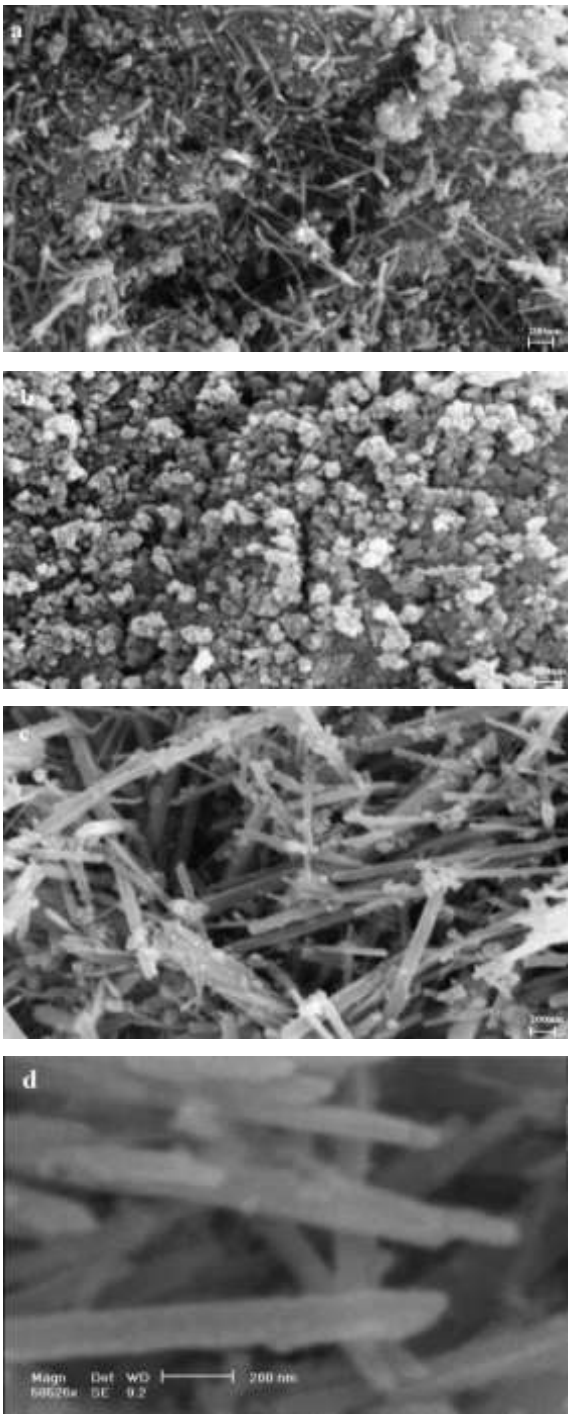

Fig.1. SEM images of manganese oxide nanowires.

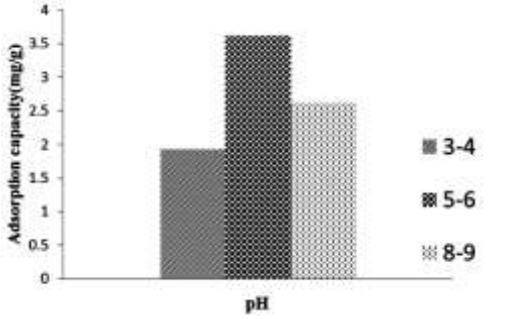

Fig. 2. Adsorption capacity at different pH.

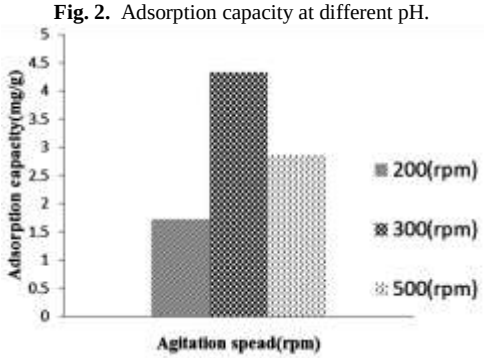

Fig. 3. Adsorption capacity at different agitation speed.

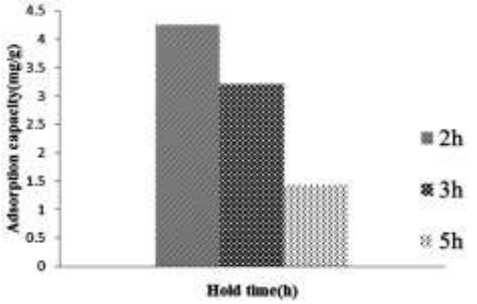

Fig. 4. Variation of adsorption capacity versus different hold time.

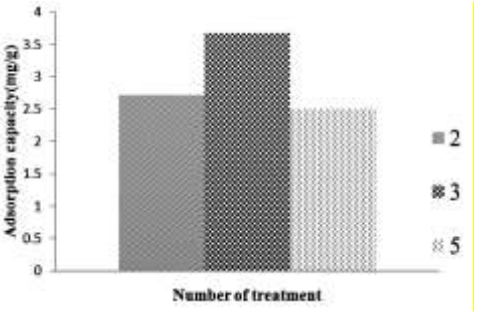

Fig. 5. Nnumber of acid treatment effect on MnO_2 adsorption capacity.

Table 3. Adsorption results of gold ions from aqueous solution.

Parameters	Number of treatment	Hold time	Agitation speed	pH	Percentage of adsorption	Adsorption capacity(mg/g)
Experiment						
T1	5	3	200	8-9	15.2	1.14
T2	3	2	500	8-9	59.8	4.49
T3	5	5	500	3-4	7.6	0.57
T4	2	5	300	8-9	29.3	2.20
T5	3	3	300	3-4	66.3	4.97
T6	3	5	200	5-6	20.7	1.55
T7	2	2	200	3-4	32.6	2.45
T8	5	2	300	5-6	77.2	5.79
T9	2	3	500	5-6	46.7	3.50

influenced by the response variable at the respective confidence level [23,24].

Results of ANOVA data, which are shown in Table 4, indicate that the pH is the most significant adsorption process parameter due to its highest percentage contribution (44.38%) among the process parameters.

Whereas hold time in the range studied has not considerable effect on the gold adsorption. Therefore, this parameter can be pooled and ANOVA table is changed to Table 5.

Table 4. Results of the analysis of the variance (ANOVA table)

Process parameter	Sum of squares	Variance	F-ratio	Percentage of contribution
Number of treatment	912.41	1046.19	-	19.35
Hold time	787.49	393.76	-	16.7
Agitation speed	922.35	461.18	-	19.56
pH	2092.38	1046.19	-	44.38
Error				
Total	4714.62	-	-	%100

Table 5. ANOVA data for the experiments.

Process parameter	Sum of squares	Variance	F-ratio	Percentage of contribution
Number of treatment	912.41	1046.19	2.6569	19.35
Hold time	(787.49)	-	Pooled	-
Agitation speed	922.35	461.18	1.1712	19.56
pH	2092.38	1046.19	2.6569	44.38
Error	787.49	393.76		16.7
Total	4714.62	-	-	100

According to the Table 5, the percent contribution due to unknown and uncontrolled factors error is low value (16.7%). A high error value indicates that some important factors are definitely omitted and experimental conditions are not precisely controlled [22]. Thus, it could be assumed that hold time factor which is not considered in Table 5, did not vary under the experimental conditions and the experiments are carried out under controlled conditions.

4. Comparison of gold ions adsorption with literature

The adsorption of gold ions by manganese oxide at optimal operating conditions is compared to the carbon material adsorbents in Table 6. As shown in this Table, the capacity adsorption of manganese oxide is comparable to activated carbon.

Therefore, manganese oxide nanowire adsorbent that was synthesized in this work can be an effective nanoadsorbent for extracting gold form diluted jewellery wastewater solutions.

Table 6. Comparison of gold adsorption with different adsorbents.

Type of adsorbent	Q (mg Au/gr adsorbent)	References
HSAS carbon	5.56	[25]
Gold C	5.28	[25]
Oil C	5.20	[25]
CECAC	6.39	[26]
Hard shell of apricot stones	2.5	[26]
2-Mercaptobenzothiazole-bonded silica gel	4.5	[27]
Manganese oxide	5.79	This work

5. Conclusion

In this research, MnO_2 nanowire adsorbent was synthesized and different adsorption parameters such as hold time, number of acid treatment, pH and agitation speed on the gold adsorption capacity via Taguchi method were studied. The results are as follows:

A Taguchi analysis of the data shows the optimal operating condition was achieved using manganese oxide with three treatments at pH 5.5 and an average speed of mixing 300 rpm. Under the optimal operating conditions, 77.2% of gold ions were adsorbed onto manganese oxide during 2h. Results of ANOVA data indicate that pH is significant adsorption process parameter due to its highest percentage contribution (44.38%). Also, hold time in the range studied has not considerable effect on gold adsorption.

References

[1] M. Ferrini, A. Manni, P. Massacci, Characterization and sampling of jewellery waste in Italy. In Proc. Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment. EnviroAnalysis 98, Ottawa, (1998a) 529.

[2] M. Ferrini, A. Manni, P. Massacci, Chemical analyses by ICP-AES of Jewellery waste in Italy. In Proc. Second Biennial International Conference on Chemical Measurement and Monitoring of the Environment. EnviroAnalysis 98, Ottawa, (1998b) 501.

[3] K.G. Neoh, K.K. Tan, P.L. Goh, S.W. Huang, E.T. Kang, K.L. Tan, *Polymer*, **40** (1999) 887.

[4] W. Liu, P. Yin, X. Liu, X. Dong, J. Zhang, Q. Xu. *Chem. Eng. Res. Des.* **91** (2013) 2748.

[5] T. Kinoshita, S. Akita, S. Ozawa, S. Nii, F. Kawaizumi, K. Takahashi, *J. Min. Mater. Char. Eng*. **2** (2003) 71.

[6] Y. Ran, J. Fu, A.W. Rate, R.J. Gilkes, *Chem. Geo.*, **185** (2002) 33.

[7] M.A.A. Schoonen, N.S. Fisher, M. Wente, *Acta*, **56** (1992) 1801.

[8] N. Tsuchida, D.M. Muir, *Metall. Trans*. **17B** (1986) 523.

[9] C.P. Gomes, M.F. Almeida, J.M. Loureiro, Sep. Purif. *Technol.* **24** (2001) 35.

[10] T. Kuwabara, H. Hirama, A. Yazawa, *J. Mining Mater. Process. Inst. Jpn*. **110** (1994) 15.

[11] F. Relth, AusIMM Bull. Nov/Dec (2003) 60.

[12] N. Saadatjoo, H. Heydari, A. Abdullahi, M. Behzad, *Journal of Applied Chemistry*, **8** (2013): 55.

[13] B. Davodi, M. Jahangiri. *Synthetic Metals*, **194** (2014): 97.

[14] M. Jahangiri, A. Rahimour, S. Nemati, M. Alimohammady, *accepted for publication in Cellulose Chemistry and Technology*, 2014.

[15] J.E. Post, *Proceedings of the National Academy of Sciences*, **96** (1999) 3447.

[16] R. Roy. *A primer on the Taguchi method*. Van Nostrand Reinholds., 1990.

[17] Montgomery, Douglas C. John Wiley & Sons, 2008.

[18] M. Anbia, F. M. Nejati, M. Jahangiri, A. Eskandari and V. Garshasbi, *J. Sci. I.R.Iran.* **3** (2015) 213.

[19] M. Jahangiri, F. Kiani, H. Tahermansouri, A. Rajabalinezhad, *J. Mol. Liq.*, **212** (2015) 219.

[20] N. Badrkhani, M. Khajenoori, A. H. Asl. *Journal of Applied Chemistry*, **7** (2013) 51.

[21] M. Khajenori, A. H. Asl. *Journal of Applied Chemistry*, **11** (2016) 151.

[22] R. A. Fisher, Breakthroughs in Statistics. Springer New York, 1992. 66.

[23] R. K. Roy, Society of Manufacturing Engineers, 2010.

[24] F. R. Aylmer. Genesis Publishing Pvt Ltd, 1925.

[25] M. Soleimani, T.Kaghazchi, *Bioresource Technol.*, **13** (2008): 5374.

[26] M. Soleimani, T.Kaghazchi, *Chem. Eng.Technol.*, **5** (2007): 649.

[27] Pu, Qiaosheng, et al., *J. Anal. Spectrom.*, **4** (1998): 249.